



Housing and Building National Research Center

HBRC Journal<http://ees.elsevier.com/hbrcj>

Phosphate removal from aqueous solution using slag and fly ash

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Received 13 November 2012; accepted 20 February 2013

KEYWORDS

Adsorption;
Slag;
Fly ash;
Phosphate;
Sorption isotherms

Abstract The application of low cost materials in wastewater treatment has recently attracted great interest; fly ash and slag have improved high performance as a low cost material and have been used as a potential adsorbent for removal of phosphate, heavy metals and organic pollutants in wastewater treatment. Batch adsorption experiments were performed in order to evaluate phosphate removal efficiency of slag and fly ash. The effect of various operating variables, i.e. initial pH, adsorbent dose, initial metal ion concentration, and adsorption time of phosphate using the slag and fly ash, has been studied. The sorption process was relatively fast and equilibrium has been reached at 30 min contact time and the maximum removal percentage was achieved at an adsorbent loading weight of 0.5 gm/100 ml. Phosphate removal ratio using slag and fly ash was 93% and 95%, respectively, under the batch test conditions. The overall uptake for the slag was maximum at pH 5 and at pH 7 for fly ash. The sorption data were represented using Freundlich and Langmuir parameters, where the sorption data were better represented by the Freundlich isotherm than by the Langmuir. The optimized method was applied for phosphate removal from wastewater of Proctor and Gamble (P&G) Company for household products. The achieved phosphate removal efficiency was 96.15% and 96.9% using slag and fly ash respectively.

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Introduction

Removal of phosphate from wastewater by chemical precipitation and advanced biological treatment has been widely investigated [1]. Among a variety of removing techniques,

adsorption is known to be more useful and economical [1]. Fly ash and slag have been used as a potential adsorbent for removal of phosphate, heavy metals and organic pollutants for water pollution control or wastewater treatment [2].

Phosphate discharged into the surface waters stimulates the growth of aquatic micro and macro organisms in nuisance quantities, which in excess can cause eutrophication in stagnant water bodies. Therefore, wastes containing phosphates must meet the discharge limits for phosphates, which are 0.5–1.0 mg/l. In order to meet effluent quality standards, a further treatment of secondary effluent is required. In wastewater treatment technology, various techniques have been used for

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phosphate removal. Among these, chemical and biological methods have been successfully applied.

The concentration of heavy metals in various wastewater samples was quite low if these nonspecific metals pollution [3]. Thus the amount of metals that would enter the soil upon applying such wastewater for irrigation would be considerably lower than permitted under the irrigation water standards suggested by the National Academy of Engineering (1972) [4]. Adsorption is one of the techniques, which is comparatively more useful and economical for such removal. The application of low cost and easily available materials in wastewater treatment has been widely investigated during recent years. Chemical treatment is widely used for the removal of phosphate. Lime, aluminum sulfate (alum), and ferric chloride are the common precipitants used for removal. However, successful results were obtained by using powdered aluminum oxide [5], slag [6], fly ash [7], half-burned dolomite [8], tamarind nut shell activated carbon [9], activated red mud, and activated alumina.

The removal of phosphate ion from aqueous solution was compared with fly ash, slag and ordinary Portland cement (OPC) and related cement blends [2]. The rate and efficiency of $\text{PO}_{4.3}$ removal were found to increase in the order: fly ash, slag, OPC, apparently mimicking the order of increasing percent Ca_2O in the adsorbents. Blending OPC with fly ash or slag evidently resulted in diminished $\text{PO}_{4.3}$ removal efficiency. Recently, [3] researchers have investigated the removal of phosphate on different fly ash.

Given the importance of water treatment of these elements, filtration, adsorption, reverse osmosis, solvent extraction, and membrane separation techniques are used for the removal of heavy metals in aqueous solution [10–12]. But the cost of these processes is an important factor in the selection process. Therefore, the use of a cheap material, which is a product of an industry has become an important way to handle wastewater treatment. Industrial by-products such as fly ash [13], waste iron [14], metallic iron [7], and hydrous titanium oxide [15], are inexpensive and abundantly available. They can be chemically modified to enhance their removal performance.

This study was aimed to examine the adsorption behavior of phosphate ions on fly ash and slag under different operating conditions to determine the optimum condition to remove phosphate.

Materials and methods

Materials

Batch adsorption experiments were performed using the following main components;

- Preparations of the adsorbents
- Simulated solution of phosphate ions and true wastewater.

Adsorbate (artificial solution)

Phosphate solution has been prepared and used in the laboratory.

Simulated stock solution of phosphate ions (1000 mg/l) was prepared by dissolving the required quantity of an annular

grade of the respective salt in the distilled water. The salt used is: anhydrous potassium dihydrogen phosphate KH_2PO_4 (0.2195 g).

Adsorbent media

In this study two types of media (adsorbent) were used, fly ash and slag. Main consistent, primary source, physical structure, chemical characterization, and primary use of each medium are shown in Tables 1–3.

Preparation of phosphate solutions and analytical methods

The salt used is: Anhydrous Potassium dihydrogen phosphate KH_2PO_4 (0.2195 g) and stock solutions further diluted with distilled water to desired concentrations of 0.1, 0.5, 1, 2, 3, 4, 5, 10, 15, 20 and 25 mg/l were prepared. Phosphate was determined by using the molybdate blue method according to standard methods for the examination of water and wastewater [16]. Ammonium molybdate reacts with phosphate to give molybdo phosphoric acid which is reduced by stannous chloride to give molybdenum blue measured at 690 nm.

All the chemicals and reagents used in this study were of analytical grade. All glassware and sample bottles were soaked in diluted HCl solution for 12 h, washed and then rinsed four times with deionized water. Deionized water was used for the preparation of solutions. All experiments were conducted in duplicate and the average values were used for data analysis.

In order to widen the applicability of the proposed method, it was tested for the removal of phosphate from: – Industrial wastewater.

Industrial wastewater

Industrial wastewater samples were collected from the effluent of Proctor and Gamble P&G company for household products, El-Giza Governorate, Egypt. Table 4 shows physico-chemical analysis of the industrial wastewater samples.

Experimental methodology

Kinetics of adsorption

Batch adsorption experiments were carried out by shaking a series of bottles containing various amounts of each low cost adsorbent (e.g. 0.1–3 g adsorbent) which was equilibrated with 100 ml of the phosphate ion solution of a known concentration (0.1–25 mg/l) in 250 ml Erlenmeyer flasks and shaken at 60–200 rpm at a room temperature of $27 \pm 2^\circ\text{C}$ for a known period (5–120 min) of time. The pH of the slurry was adjusted to a desired value in the range of 3–12 and was agitated in a shaking bath at $27 \pm 5^\circ\text{C}$ with an initial phosphate concentration of 25 mg/l.

Adsorption isotherm models

This study used both Langmuir and Freundlich isotherm equations to determine the type of adsorption.

The Langmuir adsorption isotherm equation is represented in linear equation (Metcalf and Eddy, Eq. (1))

$$1/q = 1/Q' + 1/bQ' + 1/Ce \quad (1)$$

Table 1 Main consistent, primary source and physical structure of fly ash and slag.

Adsorbent	Consistent	Source	Physical structure
Fly ash	A particulate material produced from combustion of coal in power plants	Bituminous coal-burning power plant	Spherical shape and pozzolanic properties
Slag	Iron slag is generated from Blast Furnace (BF slag) in the iron production	Iron production plants	220–370 kg slag per ton of iron being produced

where q = amount of adsorbate adsorbed per unit weight of adsorbent (g/mg); Q' = constant related to the energy or net enthalpy of adsorption; b = amount of adsorbate adsorbed per unit weight of adsorbent (mg/g); C_e = concentration of adsorbate in solution at equilibrium (mg/l).

The Freundlich isotherm model describes a multi-layer adsorption with the assumption of heterogeneous surface in which the energy, a term in the Langmuir equation varies as a function of the surface coverage. The linearized form can be represented as

$$\log q = \log K + 1/n \log C_e \quad (2)$$

where q = amount of adsorbate adsorbed per unit weight of adsorbent (mg/g); K = equilibrium constant indicative of adsorption capacity; n = adsorption equilibrium constant; C_e = concentration of adsorbate in solution at equilibrium (mg/l).

The Langmuir and the Freundlich models were used to describe the adsorption isotherm.

Results and discussion

Effect of pH

The removal of heavy metals from the aqueous solution containing a known concentration of phosphate ions according to the variation in pH is presented in Fig. 1.

The results show that, in all cases the ability to remove phosphate ions increased with increasing of pH values up to 7 for fly ash with maximum removal percent 83% and pH values up to 5 for slag with maximum removal percent 99.9% then decreased with the increasing of pH reaching 45% for fly ash and 99.7% for slag at pH values 12. Now, we can explain these results according to the crystalline structure of this fly ash and slag capsulated by inert surface in acidic medium [17,18]. This surface is destroyed at high pH and the activity of fly ash and slag particles decreased [19,20].

Effect of contact time

The effect of time on the adsorption of phosphate ions by fly ash and slag was studied by taking 0.1 mg/l sorbent with 3 mg/l phosphate in different stoppered flasks. The flasks were shaken for different time intervals in a temperature controlled shaker.

Fig. 2 shows the effect of contact time on adsorption of phosphate using both sorbents. The results show that the percentage of phosphate ion adsorption by both sorbents increased with increasing time. The uptake is rapid in the first 30 min of contact period. Beyond the 60 min contact time, the amount of phosphate adsorbed on the fly ash and slag

Table 2 Chemical composition of fly ash.

Element	Quantitative composition (%)
SiO ₂	68.01
Al ₂ O ₃	1.34
Fe ₂ O ₃	0.25
CaO	5.77
MgO	2.39
Na ₂ O	0.76
K ₂ O	2.09
SO ₅	1.44
TiO ₂	0.07
P ₂ O ₅	0.39
L.OI*	17.25
Total	99.76

Table 3 Chemical composition of slag.

Element	Quantitative composition (%)
SiO ₂	17.57
Al ₂ O ₃	2.31
Fe ₂ O ₃	7.22
FeO	12.09
CaO	48.43
MgO	7.84
Na ₂ O	0.13
KO ₂	0.038
TiO ₂	1.15
P ₂ O ₅	1.87
MnO	0.87
Total	99.7

LOI = loss on Ignition.

remains constant as shown in Fig. 2. These data indicate that, the equilibrium is attained after 60 min. The industrial of adsorbent and the available adsorption sites affect the rate of adsorption of phosphate. The mechanism of solute transfer

Table 4 Physico-chemical analysis of industrial wastewater sample.

Parameters	Result
pH	10.25
COD mg/l	560
BOD ₅ mg/l	190
Ammonia mg/l	14.2
Nitrite mg/l	24
Nitrate mg/l	32
Total phosphate mg/l	40

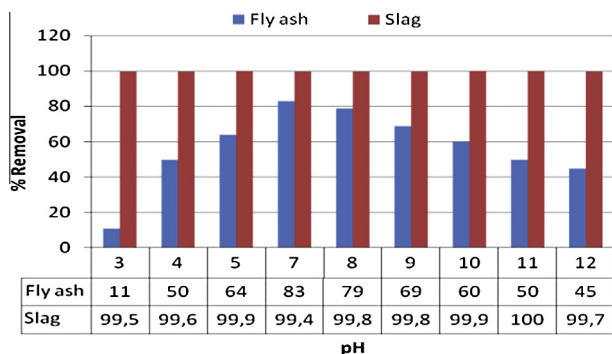


Fig. 1 Effect of initial pH (initial concentration of phosphate, 3 mg/l; fly ash and slag dosage, 0.1 mg/l; contact time, 120 min, rpm 180).

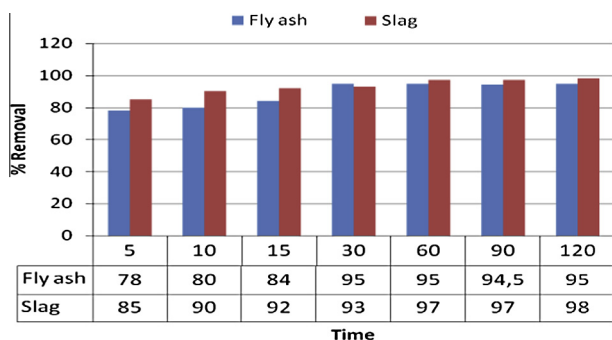


Fig. 2 Effect of contact time (initial concentration of phosphate, 3 mg/l; fly ash and slag dosage, 0.1 mg/l; pH, 7 and 5, rpm 180).

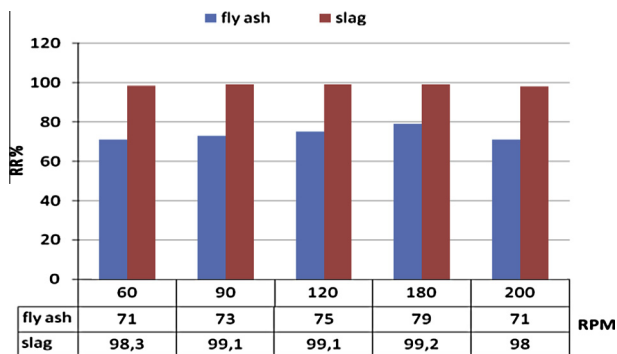


Fig. 3 Effect of agitation speed (initial concentration of phosphate, 3 mg/l; fly ash and slag dosage, 0.1 mg/l; contact time, 120 min, pH 7 and 5).

to the solid includes diffusion through the fluid film around the adsorbent particle and diffusion through the pores to the internal adsorption sites. In the initial stages of adsorption of phosphate, the concentration gradient between the film and the available pore sites is large, and hence the rate of adsorption is faster. The rate of adsorption decreases in the later stages of the adsorption probably due to the slow pore diffusion of the solute ion into the bulk of the adsorbent [18,20], and it reached the plateau value at about 120 min for phosphate (see Fig. 3).

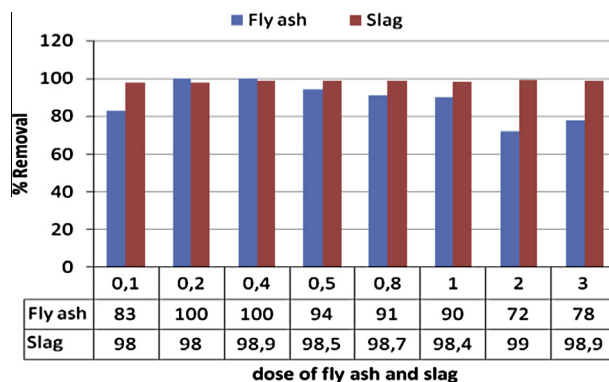


Fig. 4 Effect of fly ash and slag dosage (initial concentration of phosphate, 3 mg/l; pH 7 and 5; contact time, 120 min, rpm 180).

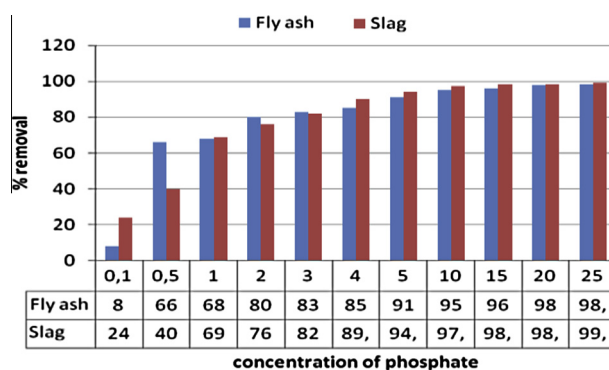


Fig. 5 Effect of initial influent phosphate ion concentrations (fly ash and slag dosage 0.4 mg/l, pH 7 and 5, rpm 180 and contact time 120 min).

Effect of mixing speed

Adsorption studies were carried out with a magnetic shaker at an initial concentration of phosphate of 3 mg/l; fly ash and slag dosage was 0.1 mg/l with contact time 120 min and pH 7 for fly ash and 5 for slag. The agitation speed varied from 60 to 200 rpm. It was observed that the adsorption percentage of phosphate ion onto the fly ash increased with increasing agitation speed reaching a maximum of 79% for fly ash and 99.2% for slag at 180 rpm then decreased with the increasing of agitation speed reaching 71% and 98% at 200 rpm.

It found that the removal of metal ions increased with increases in rpm to some extent. This is due to dispersal of the adsorbent particles in the aqueous solution which leads to reduced boundary mass transfer and even then it may increase the velocity of particles, so that it increases the percent removal of metal ions [21].

Effect of fly ash and slag dosage on adsorption

Fig. 4 shows the adsorption capacity of phosphate as a function of fly ash and slag. The effect of both adsorptions on the sorption kinetics of phosphate ion was studied at pH of 7 for fly ash and 5 for slag, 3 mg/l initial phosphate ion concentration. The sorbent dose was varied between 0.1 and 3 mg/l.

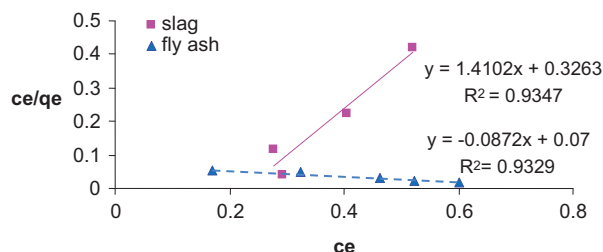


Fig. 6 Langmuir plot for phosphate adsorption onto natural fly ash and slag.

This result is expected because the increase of adsorbent dose leads to a greater surface area. When the adsorbent concentration was increased from 0.1 to 0.4 g/100 ml, the percentage of phosphate ion adsorption increased from 83% and 98% to 100% and 98.8%. At a higher dosage, the equilibrium uptake of phosphate ions did not increase significantly with increasing fly ash and slag dosage. Such behavior is expected due to the saturation level attained during an adsorption process. This finding agrees with Koumanova et al. [22]. For subsequent studies, a dose of 0.4 g/100 ml of fly ash and slag was selected.

Effect of concentration of phosphate

The initial metal concentration provides an important driving force, hence a higher initial concentration of phosphate ions increases the sorption rate. The effect of changing the initial concentration of phosphate ion on adsorption, while keeping the dosage of slag and fly ash constant at room temperature and equilibrium pH values is illustrated in Fig. 5. These plots showed that the total metal ion adsorbed increased sharply in the beginning and then slowly toward the end of the run. For the different initial concentrations, adsorption equilibrium was rapidly achieved. As shown in Fig. 5 with the increase of the initial concentration of phosphate from 0.1 to 25 mg/l, the percentage removal for the slag increases from 76% to 99% and for fly ash the percentage removal increases from 80% to 98.1% in the range of 1–25 mg/l initial phosphate concentration. The increase in the percentage removal of phosphate can be explained with the fact that, the higher adsorption rate is related to the utilization of all active sites available for the adsorption at a higher concentration [23,24] (see Fig. 6).

Table 5 Physico-chemical analysis of influent P&G Company before and after treatment with industrial wastes.

Parameter	Influent (mg/l)	Slag	%	Fly ash	%
pH	10.25	9.96	–	10.08	–
COD mg/l	560	400	28.5	340	39.2
BOD ₅ mg/l	190	109	42.65	156	17.8
Ammonia mg/l	14.2	10.5	26.05	12.4	12.6
Nitrite mg/l	32	15	53.1	27	15.6
Phosphate mg/l	40	1.55	96.15	1.21	96.9
TDS mg/l	1680	1355	19.35	1060	36.9
Chloride mg/l	189	132	30.15	141	25.3
Sulfate mg/l	750	621	17.2	452	39.7
Oil and grease mg/l	30	11	63.35	10	66.6

Batch isotherm studies

Equilibrium data are basic requirements for the design of adsorption systems and are used for the mathematical description of the adsorption equilibrium of the metal ion on the adsorbent. The results obtained on the adsorption of phosphate were analyzed by Langmuir and Freundlich [1]. For the sorption isotherms initial metal ion concentration was varied while the pH of solution and adsorbent weight in each sample held constant. The sorption data for the removal of phosphate ion have been correlated with the Freundlich and Langmuir models. Fig. 7 and Fig. 8 represent this relation in the presence of slag and fly ash. The high value of coefficient of determination ($R^2 = 0.9347, 0.9329$) for slag and fly ash obtained indicates a good agreement between the experimental values and isotherm parameters but, negative values for the Langmuir isotherm constants indicate the inadequacy of the isotherm model to explain the adsorption process [6].

Freundlich model has a limited application for slag and fly ash sorption with a correlation coefficient, $R^2 = 0.8799, 0.9493$. The best fit to the Freundlich model was obtained for fly ash adsorption, with a correlation coefficient 0.9493.

Treatment of metal industrial wastewater

Based on the promising results of phosphate removal from aqueous solutions, tests were conducted to evaluate these results using real wastewater. The wastewater used was taken from P&G. The effect of slag and fly ash on the removal of

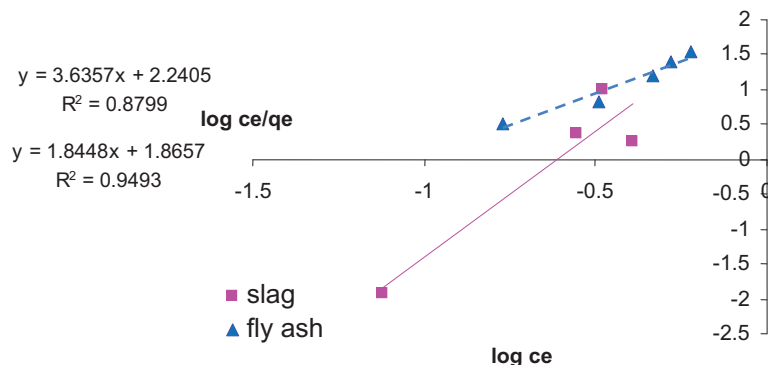


Fig. 7 Freundlich plot for phosphate adsorption onto natural fly ash and slag.

COD, BOD₅, Ammonia, Nitrate phosphate, TDS, TS, Chloride and Sulfate is depicted in Table 5.

The results show that, 28.5%, 39.2% of COD was removed, 42.65%, 17.8% of BOD₅ was removed, 26.05%, 12.6% of ammonia was removed, 53.1%, 15.6% of Nitrate was removed, 96.15%, 96.9% of phosphate was removed, 19.35%, 36.9% of TDS was removed, 30.15%, 25.3% of chloride was removed, 17.2%, 39.7% of Sulfate was removed and 63.35%, 66.6% of oil and grease was removed.

Conclusion

1. Fly-ash collected from the thermal power station and slag from the iron industry are effective adsorbents as compared to costlier conventional powdered activated carbon for the removal of phosphate ion from aqueous solution.
2. The results show that the removal efficiency will remain high at lower initial concentration and then increases as the initial concentration is further increased.
3. The results of the tests using real wastewater showed that fly ash was effective in the simultaneous removal of phosphate in metal industrial wastewater.
4. Phosphate adsorption by slag and fly ash increased with the increase in pH and reached a maximum in the pH range of 5–11. For slag it was found that the amount of phosphate adsorbed at pH 5 was the greatest. Fly ash, reached maximum phosphate adsorption at neutral pH value 7.
5. The low cost adsorbent may also lead to less environmental problems. Improvement in plant economics may also be expected.

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